ON THE RAMAN SPECTRA OF *n*-PROPYL BROMIDE AND ETHYLENE CHLORHYDRIN IN DIFFERENT STATES*

By B. M. BISHUI

(*Received for publication, June 2, 1948*)

Plate XIII

ABSTRACT. The Raman spectra of *n*-propyl bromide and ethylene chlorhydrin in the liquid and solid states as well as the polarisation of the Raman lines of the liquids have been investigated. Some intense Raman lines are observed to disappear when *n*-propyl bromide is solidified as observed in the case of *n*-propyl chloride by previous workers, but such disappearance of some Raman lines in the case of ethylene chlorhydrin observed by those authors could not be confirmed. The hypothesis put forward by those authors that such a disappearance of the lines is due to the presence of only single molecules of one configuration in the solid state and of two different configurations in the solid state is shown to be unsatisfactory. An alternative hypothesis based on the assumption that the halogen atom of one propyl halide molecule forms a virtual bond with a carbon atom of a neighbouring molecule is put forward to explain the observed changes in the Raman spectra.

INTRODUCTION

The Raman spectra of *n*-propyl chloride and ethylene chlorhydrin were studied formerly by Mizushima, Morino and Nakamura (1940) and they observed that some of the prominent Raman lines due to the liquid state disappear completely when these substances are solidified. They explained the results on the hypothesis that the liquid state consists of two types of molecules, while the solid state contains only one type of molecules. It was, however, argued by them that since the lines disappearing in the case of *n*-propyl chloride are not analogous to those disappearing in the solid state in the case of ethylene chlorhydrin, the configurations of the molecules in the solid state of these two substances are different from each other.

They concluded that the solid ethylene chlorhydrin contains molecules of trans configuration and molecules of solid *n*-propyl chloride have their C-Cl group rotated through 120° from the trans configuration (gauche form). On the other hand, if the results observed with ethylene dichloride and *n*-propyl chloride are compared with each other it can be seen that analogous lines, *e.g.*, the lines 654 cm^{-1} and 649 cm^{-1} due to the C-Cl valence oscillation disappear in the solid state in the two cases respectively. Therefore the configuration of the molecules which produces these lines should be the same in the two cases, *i.e.*, if in the former case the Cl-C-C-Cl chain lies in one plane the C-C-C-Cl chain should also do so in the latter case. Since

* Communicated by Prof. S. C. Sirkar.

Mizushima and Morino (1938) conclude that the ethylene dichloride molecules in the solid state are of trans configuration and Mizushima, Morino and Nakamura (1940) have pointed out that molecules of *n*-propyl chloride in the solid state are of gauche configuration—their explanation of these observed facts does not seem to be satisfactory. The question has therefore been re-investigated by studying the Raman spectra of *n*-propyl bromide and ethylene chlorhydrin at different temperatures and states. The Raman spectra of *n*-propyl bromide in the liquid state have also been studied at the room temperature and at about $-80^{\circ}C$ to find out whether the disappearance of the lines in the solid state is a continuous process or it depends on the nature of the states alone, because according to the hypothesis put forward by Mizushima *et al* (1940) the intensity of the line 649 cm^{-1} should be dependent on temperature alone. Further, the Raman spectra of solutions of *n*-propyl bromide in *n*-hexane, carbontetrachloride, benzene and toluene have been studied in order to find out whether some of the lines undergo any change in intensity in the solution. The Raman spectra of ethylene chlorhydrin in the liquid state at the room temperature and in the solid state at about $-170^{\circ}C$ have also been studied in order to verify the results reported by Mizushima, Morino and Nagamura (1940). The polarisation of the Raman lines of both the substances have been studied in order to understand the significance of the changes which are observed in the Raman spectra with the change of temperature and state of these substances.

EXPERIMENTAL

Liquids from Kahlbaum's original packing were used after being re-distilled in vacuum. The technique developed for studying the Raman spectra of substances nearly at the temperature of the liquid oxygen previously by Sirkar and Bishui (1943) was used in the present investigation. The Fuess spectrograph used has a dispersion of about 13 A.U. in the region of 4047 A.U., but as it gives a coma extending up to about 38 cm^{-1} from the centre of the unexposed Rayleigh line on its Stokes side, any weak new Raman lines having frequency shift less than 38 cm^{-1} which might have appeared in the spectra due to the substances in the solid state were masked by this coma and could not be detected. The Raman spectra of the liquids at the room temperature have also been studied by the usual method. The polarisation of the Raman lines due to the liquids was studied by photographing the horizontal and the vertical components of the scattered light simultaneously with the help of a double image prism. Inspite of the special care taken to solidify the substances slowly in order to obtain a homogeneous transparent mass, the spectrum of the scattered light showed the presence of strong continuous background due to the extraneous light, and therefore, it has not been possible to record all the faint Raman lines in the solid state. The spectrogram due to the solid ethylene chlorhydrin obtained after repeated

trials is not a satisfactory one, because when the liquid is solidified, the solid mass cracks into a number of pieces exhibiting different facets and the whole spectrum is masked by the irregular scattering from these facets. It has, however, been possible to verify the broadening of certain strong lines in the solid state.

TABLE I

n-Propylbromide ($CH_3CH_2CH_2.Br$)

Liquid State			Solid State
At room temp. Present author.	Harkins, & Bowers (1931)	At about −80°C Present author	At about −170°C Present author.
			60 (2) k
			92 (1) k
225 (2) e, P			227 (1) e, k
317 (8) e, k; P	312 (2) 459 (2)	317 (1)	308 (2) e, k
568 (10) e, k, P	563 (1)	568 (3)	v
651 (5) e, k, P	648 (2)	651 (1)	638 (2) e, k
776 (3) e, k; P	778 (1)		
848 (3) e, k, P			
884 (2) e, k, P			
976 (1) e, k, P			
1024 (8) e, k; P	1023 (2) 1143 (2)	1020 (1)	1020 (3) e, k
1228 (3) e, k, P	1165 (2) 1185 (2)		
1315 (1) k; P	1229 (2) 1435 (1)		
1462 (5) e, k, D		1462 (1)	1462 (1) e, k
2850 (3) e, k, P			2854 (1) e, k
2870 (2) e, k, P	2896 (2)		
2902 (3) e, k, P	2933 (2)	2937 (1)	
2937 (3) e, k, P			2939 (3) e, k
2968 (4) e, k; P	2965 (2) 2993 (3)	2968 (1)	2961 (2) e, k
3010 (2) e, k; D		3010 (0)	3005 (1) e, k

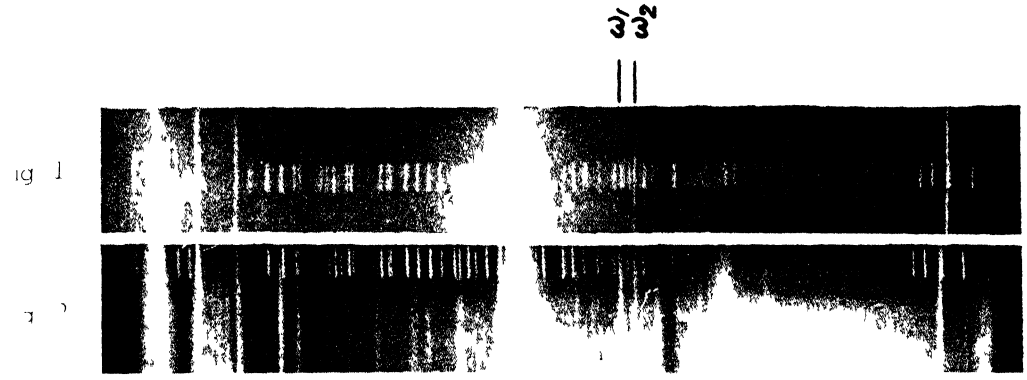
TABLE II

Ethylene Chlorhydrin ($ClH_2C.CH_2OH$).

Liquid State at room temperature		Solid State	
Muzishima *et al* (1940)	Present author	Mizushima *et al* (1940)	At about −170°C Present author.
164 (1b) e	165 (0) e, P		
296 (4) e	295 (1) e, P	311 (0) e,	
396 (5) e, k, 1	394 (1b) e, k, P		
476 (4) e, k	475 (2b) e, k, D	471 (0) e,	
662 (10b) e, k (1), f, g.	662 (5) e, k, P	659 (0) e, k, (1), f, g	660 (2) e, k
750 (7b) e, k, (1)	750 (2) e, k, P		750 (0b) e, k, ?
850 (b) e, (k)	853 (3) e, k, P	849 (3) e, (k)	850 (2) e, k
942 (6b) e, (k) ?	940 (2) e, k, D	939 (3) e, k	
1034 (7) e, k	1032 (2) e, k, P	1036 (3) e, k	
1055 (2) e, k			
1078 (4) e, k		1083 (1) e, k	
		1130 (0) e, k	
		1171 (0) e, k	
1179 (3) e, k			
1245 (5b) e, k	1242 (2) e, k, P	1246 (0) k	
1283 (3) e, k			
1298 (3) e, k			
1379 (1) e, (k)		1387 (0) e, k	
1443 (6) e, k	1430 (3) e, k, D	1424 (2) e, k	
1457 (7) e, k	1458 (3) e, k, D	1451 (2) e, k	1456 (0) e, k
2725 (3b) e, k			
2875 (7) (e) k	2885 (3) e, k, P		2884 (0) k
2925 (6) (e) k, 1	2935 (2) e, k, P	2934 (6) e, k, 1	2938 (0) k
2962 (10) e, k, i	2960 (5) e, 1, k, P	2960 (8) e, k, i	2960 (3) e, k
3011 (8) e, (k) (1)	3010 (3) e, k, D	3013 (5) e, k	3010 (2) k

RESULTS AND DISCUSSION

The spectrograms for *n*-propylbromide at different temperatures are reproduced in Figs. 1 and 2 of Plate XIII. The results obtained are given in Tables



Raman Spectra

Fig 1 *n* - Propylbromide at about 170 C
Fig 2 *n* Propylbromide at about 30 C

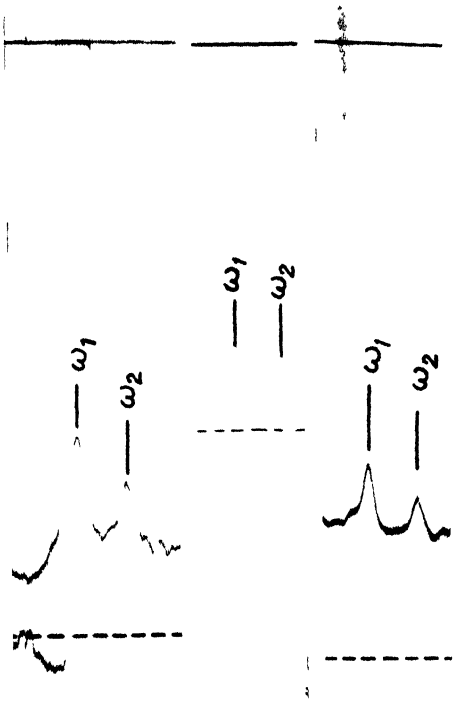


Fig 3 Fig 4 Fig 5

Microphotometric Records of Raman Spectra

Fig 3 *n* - Propylbromide at + 30°C
Fig 4 *n* - Propylbromide at 80°C
Fig 5 *n* - Propylbromide dissolved in hexane

ω_1 -- 568cm^{-1} ω_2 -- 651cm^{-1}

I and II. The first column of each table contains the results reported by some previous workers. The data for the solid at about $-170°C$ obtained in the present investigation are given in the last column. The letters P and D denote polarised and totally depolarised respectively. The approximate visually estimated intensities are given in the parentheses. The microphotometric records of the lines 568 cm^{-1} and 651 cm^{-1} of *n*-propyl bromide in the liquid state at the room temperature, at $-80°C$ and in solution in *n*-hexane are reproduced in figures 3, 4 and 5.

n-propyl bromide.—It can be seen from Table I that the line 568 cm^{-1}, which is the most intense line in the Raman spectrum of *n*-propyl bromide in the liquid state, is totally absent in the Raman spectrum due to solid *n*-propylbromide at $-170°C$. Similar phenomenon was also observed in the case of *n*-propyl chloride by Mizushima *et al* (1940). It is further observed that the ratio I_{568}: I_{651} diminishes only slightly when the liquid is cooled down to about $-80°C$. Hence the disappearance of the line 568 cm^{-1} in the solid state is due almost wholly to the change of state. The disappearance of the corresponding line 649 cm^{-1} of *n*-propylchloride in the solid state has been explained by Mizushima *et al* on the assumption that in the solid state the molecules are all of the "gauche" type while in the liquid state molecules of both gauche and 'trans' configurations are present. Here the name gauche has been given loosely to the configurations in which C-Cl line rotates through an angle of 120° from the C-C-C plane and the configuration in which C-C-C-Cl atoms lie in one plane has been called trans. It is further observed that along with the line 568 cm^{-1} and 649 cm^{-1} of *n*-propylbromide and *n*-propylchloride respectively many other Raman lines also disappear when these liquids are frozen. The hypothesis put forward by Mizushima *et al* (1940), therefore, leads to the conclusion that as the C-Cl group rotates through 60° from the plane of C C-C group in propyl chloride, the frequencies of many modes of vibration of the C-C-C group become different from those of the corresponding vibrations of the trans configuration. Since the Cl atom is attached to one end of the molecule, it is difficult to understand how the rotation of C-Cl group can affect the frequency of vibration of the C-C group at the other end. Further, the number of lines below 1100 cm^{-1} due to the different modes of vibrations of the C-C-C-Cl group of *n*-propyl chloride in the solid state is only four and in the liquid state it is about twelve. Hence according to the hypothesis put forward by Mizushima *et al* the gauche configuration gives four Raman lines with frequency shifts below 1100 cm^{-1} and the trans configuration yields eight such lines. This is highly improbable and the explanation does not seem to be correct. In the case of *n*-propyl bromide also similar difficulty arises, the number of corresponding lines in the solid and liquid states being four and nine respectively. Of course, there are two new Raman lines at 60 cm^{-1} and 92 cm^{-1} in the case of solid propyl bromide, but those are not due to any intramolecular vibration of the single molecule but may be due to vibration of strongly associated molecules. It

has also been observed by the present author (Bishui, 1948) that in the case of both 1, 1-dichloro-ethane and 1, 2-dichloro-ethane in the liquid state the number of lines having frequency shifts below 1100 cm^{-1} is ten. Since the former molecule (H_3C-CCl_2H) cannot have any rotational isomer and a single molecule cannot yield more than six lines having frequency shifts below 1100 cm^{-1} we have to make an assumption other than the presence of two rotational isomers in the liquid state in order to explain the presence of a large number of Raman lines having frequencies below 1100 cm^{-1} in the Raman spectrum of 1, 1-dichloro-ethane and 1, 2-dichloro-ethane.

Again if the lines 568 cm^{-1} and 638 cm^{-1} were due to the trans and gauche configurations respectively as assumed by Mizushima *et al*, at -80°C the intensity of the line 568 cm^{-1} ought to have diminished considerably, because in the solid state all molecules are assumed to be of gauche configuration by those authors. Actually, however, the intensity of the line 568 cm^{-1} does not diminish considerably even when the liquid is cooled down to the temperature −80°C. It appears from all these facts that the assumption that in the liquid state two types of single molecules are present is not correct.

An alternative hypothesis can be suggested to explain the observed facts in the case of propyl halides. In the liquid state each molecule of *n*-propyl bromide is surrounded by a large number of similar molecules, but as the arrangement may be expected to be almost random different portions of the surrounding molecules may be adjacent to the different carbon atoms of the central molecule on which our attention is fixed now. Thus the Br atom of a neighbouring molecule may approach very close to a carbon atom of the molecule in question and may form a virtual bond. The frequency of the C-Br valence oscillation in the former molecule will be altered in such a case. The frequencies of vibrations of the C-C-C group will also be changed if a Br atom of a neighbouring molecule becomes attached to one of the carbon atoms and consequently some new Raman lines will appear. The Br atom in C-Br group of some of the molecules, however, may remain free giving thereby the normal C-Br frequency as well as the normal frequencies of the single molecule. The frequency of the C-Br valence oscillation in the methyl-bromide is 594 cm^{-1}. The frequencies of symmetric and anti-symmetric C-Br valence oscillations in CH_2Br_2 are 578 cm^{-1} and 633 cm^{-1} respectively (Trumpy 1934). In the case of *n*-propyl bromide in the liquid state there seems to be two lines due to the C-Br oscillation, the frequencies being 568 cm^{-1} and 651 cm^{-1} respectively, Of these the line 651 cm^{-1} seems to be the normal C-Br valence oscillation and the line 568 cm^{-1} due to the C-Br oscillation in the molecule in which the Br atom has formed a virtual bond with the carbon atom. In the solid state the arrangement of the molecules is regular and therefore instead of having different values as in the liquid state the intermolecular distance will have a particular value in the solid state and consequently the C-Br frequency will not be affected so much as in the liquid state in which the distance between strongly associated molecules mentioned above may be smaller than

those between other free molecules. The frequency of the C-Br valence oscillation in the solid state is none the less smaller than that in the liquid state, the difference being about 17 cm^{-1}. This is due to the influence of the neighbouring molecule on the C-Br bond and this fact definitely shows that in the liquid state if the C-Br group can approach nearer to a carbon atom of the neighbouring molecule the C-Br frequency may diminish still further, and this can explain the presence of the Raman line 568 cm^{-1} in the case of *n*-propyl bromide in the liquid state. In the solid state, therefore, neither strongly associated molecules nor free molecules are present, but the molecules are all loosely associated. From figures 3 and 5 it is seen that on dissolving *n*-propyl bromide in *n*-hexane the intensity of the line 568 cm^{-1} diminishes slightly. The ratio of the intensity of this line with that of 651 cm^{-1} was measured with the help of blackening-log intensity curve both for the pure state and for solution in *n*-hexane. The values of the ratio were found to be 5:2 and 3:2 respectively. These results corroborate the hypothesis that strongly associated molecules are responsible for the presence of the line 568 cm^{-1} in the Raman spectrum of the liquid.

Ethylene Chlorhydrin.—The results for ethylene chlorhydrin are given in Table II. The results reported by Mizushima, Morino and Nakamura (1940) for liquid and solid ethylene chlorhydrin are given in the first and the third column of Table II respectively. Samples of the liquid were taken from different old packings of Merck and Kahlbaum and when examined separately they gave the same Raman lines. Table II, however, shows that the visually estimated relative intensities of the lines 662 cm^{-1} and 750 cm^{-1} observed in the present investigation are not the same as those given by previous authors. The line 750 cm^{-1} is observed to be only about one-third as intense as the line 662 cm^{-1} and the former line is broader than the latter one. The broad and faint lines 394 cm^{-1} and 475 cm^{-1} could not be observed definitely in the spectrograms due to the solid state, but there seemed to be an indication of the presence of a broad line 750 cm^{-1} in the solid state. Thus the disappearance of the line 750 cm^{-1} in the solid state observed by Mizushima *et al* (1940) cannot be confirmed by the results obtained in the present investigation. The line becomes broader in the solid state and is therefore easily masked by the continuous background, but the line does not actually disappear. Hence the conclusions arrived at by those authors from the disappearance of this line in the solid state are not correct. In fact except some minor shifts in the positions of some of the lines and broadening of a few other lines, no other conspicuous change takes place in the Raman spectrum when ethylene chlorhydrin is solidified. In the liquid state the molecules cannot be single but are strongly associated and in the solid state also they remain so. Even in the liquid state the lines 475 cm^{-1}, 940 cm^{-1}, 1430 cm^{-1}, 1458 cm^{-1} and 3010 cm^{-1} are totally depolarised. Hence the molecule has at least one element of symmetry. The single molecule can have only a plane of symmetry. The associated molecule also may have a plane or a two-fold axis of symmetry.

ACKNOWLEDGMENT

The author is indebted to Prof. S. C. Sirkar, D.Sc., F.N.I., for his kind interest and encouragement during the progress of the work and to Prof. M. N. Saha, F.R.S., for kindly allowing him to use the microphotometer and photo-enlarger at the University College of Science, Calcutta.

INDIAN ASSOCIATION FOR THE
CULTIVATION OF SCIENCE,
210 BOWBAZAR STREET,
CALCUTTA

REFERENCES

Bishui, B. M. 1948), *Ind J. Phys.*, **22**, 319.
Harkins, D , and Bowers, E. (1931), *Phys. Rev* , **38**, 1845.
Mizushima, S , and Morino, Y. (1938), *Proc. Ind. Acad Sc. of India A.*, **8**, 315.
Mizushima, S., Morino, Y., and Nakamura (1940), *Sci. Papers. Inst. Phys. Chem Research (Tokyo)*, **37**, 205.
Sirkar, S. C., and Bishui, B. M. (1943), *Proc. Nat. Inst. Sc. of India*, **9**, 287.
Trumpy, B (1934), *Z. f Phys.*, **90**, 133.